DIRECT CHARACTERIZATION OF LATE-METAL NITRIDO COMPLEXES

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

Direct Characterization of Late-Metal Nitrido Complexes

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Late-metal nitrido complexes are highly reactive structures that participate in important synthetic reactions, such as C–H amination. The intrinsic reactivity of these complexes renders them challenging to directly characterize.[1] With the goal of utilizing late-metal nitrido complexes to oxidize small hydrocarbons, such as methane, characterization of related, highly reactive metal–ligand multiply bonded complexes is essential. We are interested in using photocrystallography to characterize reactive structures. In this experiment, the highly reactive complex of interest is generated from a stable metal azide precursor solid-state photolysis. With the use of solid-state photolysis, the highly reactive nitrido complex will essentially be stuck in its crystalline state and allow for characterization. We anticipate that this technique may allow for the direct characterization of these late-metal nitridos.

I will be working on the synthesis of a cobalt nitride complex using solid-state chemistry, combined with photocrystallographic techniques. This synthesis will require multiple steps with unique challenges along the way. If successful, the synthesis of [(BIMPN^{Mes,Ad,Me})Co^{II}(N_3)] will be completed, purified, and will generate the metal nitride complex after solid-state photolysis.

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

A terminal nitride ligand is a nitrogen atom bonded to a metal atom. Metal nitride complexes have been of interest due to their roles in nitrogen fixation, atom- and group-transfer chemistry, and catalysis.[1] Depending on the metal used to coordinate with the nitrido and the number of d-electrons of that metal, the reactivity of the nitride ligand can vary greatly. Nitrido complexes of group 6-8 transition metals have been extensively researched and synthesized. These complexes are relatively stable;[1] an example of atom transfer between manganese and chromium is described in Figure 1. However, late-metal nitridos have not been structurally characterized due to their increased relative reactivity.[1]

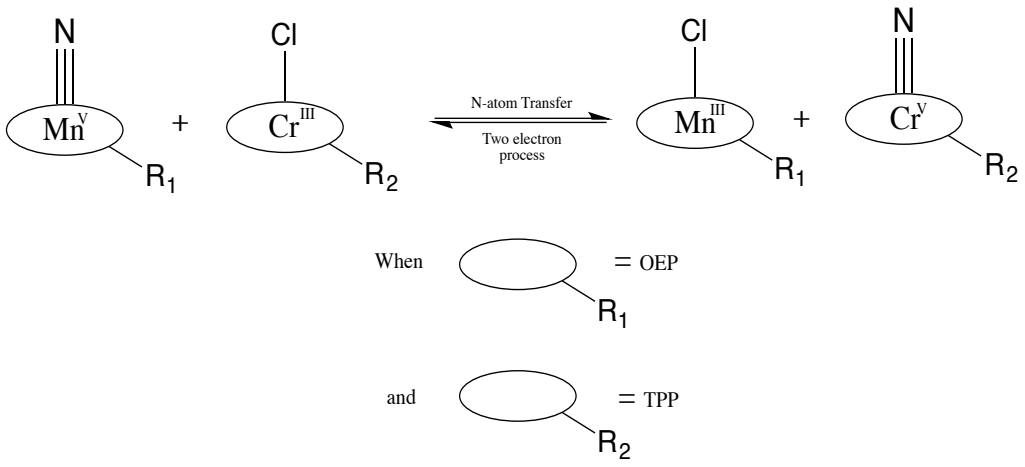


Figure 1. Homometallic nitrogen atom transfer as a two-electron process utilizing both manganese and chromium porphyrin systems and manganese salen systems. Reprinted from *Coord. Chem. Rev.* 2003, *243*, 83.

Synthesis of nitrido complexes can occur by two main methods. These methods include creating a nitrido by adding multiple bonds to an existing metal–nitrogen (M–N) bond and by forming new nitridos from known nitrido complexes.[1] Forming new nitrido complexes from known complexes implements the atom transfer capabilities of many stable nitrido complex (see Figure 1). This method does not work for all metals and resulted in the need for a new method. In 1981, Arshankow *et al.* developed the method of adding multiple bonds to an existing metal-nitrogen bond via photolysis of the corresponding metal-azide (Figure 2).[2] This sparked new research into nitrido synthesis and allowed for more metals to be used in nitrido complexes.

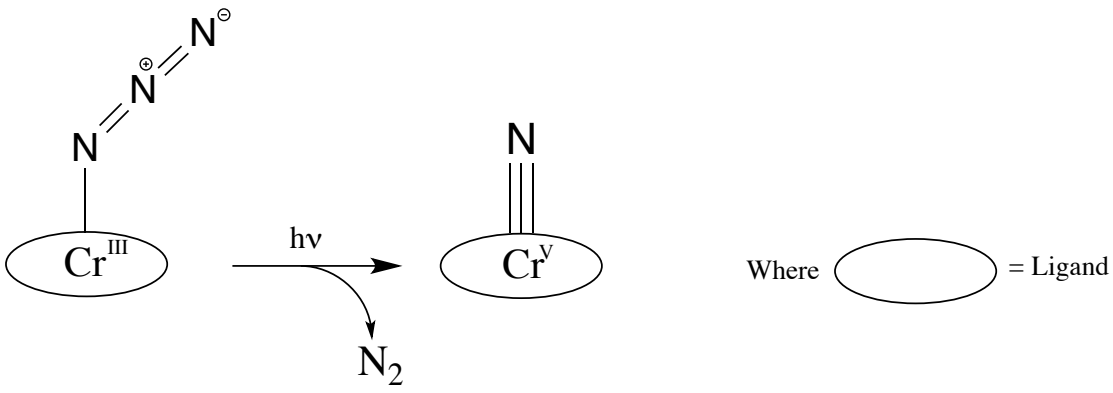


Figure 2. The chromium(V) nitrido was generated after photolysis of chromium(III) azide using a 250 W medium pressure Hg lamp. *Transit. Metal Chem.* 2004, *29*, 751

With the hopes of making a more reactive metal-nitrido, the use of a late metal is of interest. These metals (group 9 or later) will have more d-electrons. When coordinating with the nitrido, the increase in electrons will destabilize the complex. This loss in stabilization will increase the reactivity of the nitrido. The synthesis of a cobalt(IV) nitrido would give a d^5 metal, producing a relatively reactive nitrido. The specific cobalt(IV) nitrido of interest is $[(BIMPN^{Mes,Ad,Me})Co^{IV}(N)]$ (Figure 3).[4] This complex is proposed to be generated via photolysis

of [(BIMPN^{Mes,Ad,Me})Co^{II} (N_3)] (see Figure 3). Thus, the experiment conducted herein was to synthesize the [(BIMPN^{Mes,Ad,Me})Co^{II} (N_3)] (see Scheme 1).

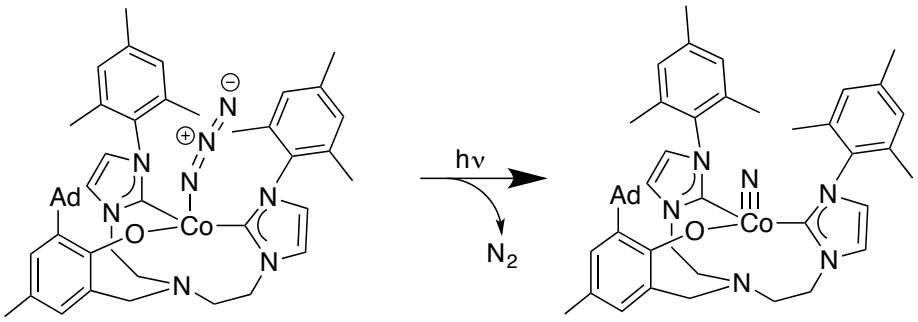
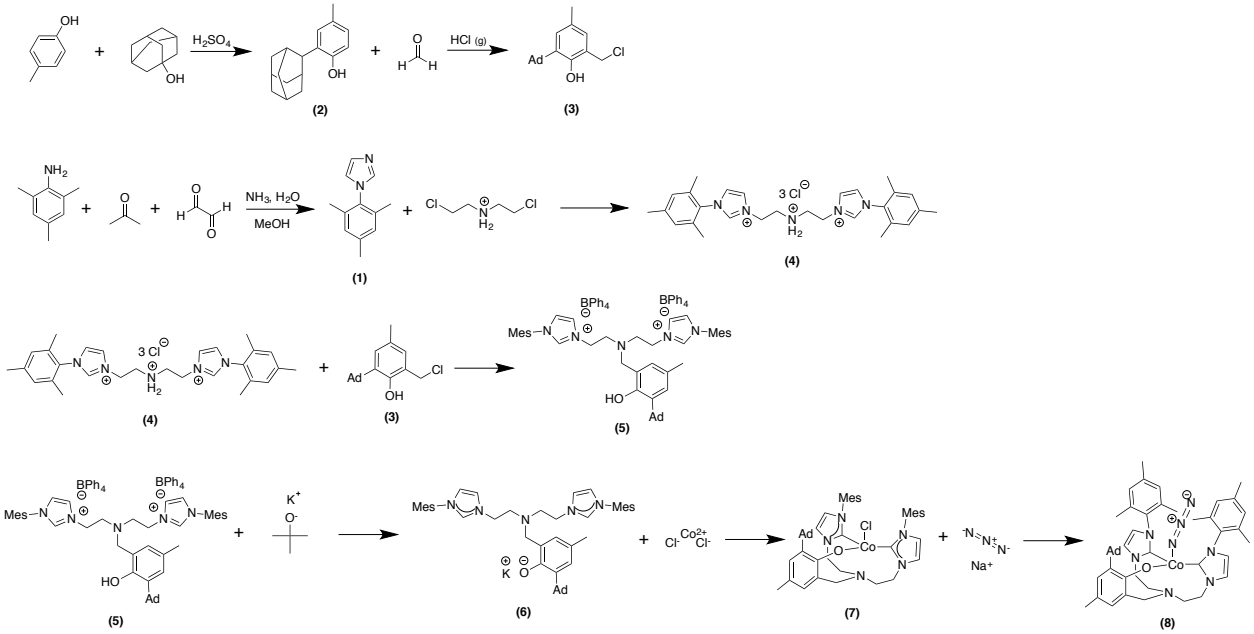


Figure 3. The photolysis of the cobalt(II) azide generates a cobalt(IV) nitrido and nitrogen gas.

Scheme 1. The complete synthesis scheme for [(BIMPN^{Mes,Ad,Me})Co^{II} (N_3)].



CHAPTER II

EXPERIMENTAL

1-(2,4,6)-trimethylphenyl-*1H*-imidazole (1)

The procedure was conducted according to the literature.[5] In a flask, 13.5 g (99.7 mmol, 1 eq) of 2,4,6-trimethylaniline and 15.2 g (262 mmol, 2.63 eq) of glyoxal were combined in 55 mL of methanol. The reaction mixture was stirred for 23 h. Then, 10.7 g (0.200 mol, 2.01 eq) of ammonium chloride and 16 mL (173 mmol, 1.74 eq) of formaldehyde (37%, aq) were added to the reaction mixture. The resulting mixture was refluxed under nitrogen, turning the mixture dark brown. After 1 h, 14 mL of phosphoric acid was added over 10 minutes. The reaction mixture was refluxed for 9 h before being concentrated. The crude concentrate was quenched by pouring over ice and neutralizing the solution with 100 mL of 40% potassium hydroxide. The mixture was extracted with diethyl ether and washed with brine and water. Concentration of the organic phase yielded a brown powder. Yield: 9.66 g (52.1%); ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 7.43 (s, 1H), 7.23 (s, 1H), 6.97 (s, 2H), 6.89 (t, 1H, J= 1.5 Hz), 2.34 (s, 3H), 1.99 (s, 6H).

2-adamantyl-p-cresol (2)

This experimental procedure was conducted according to the literature.[6] In 46 mL of dichloromethane, 5.58 g (51.6 mmol, 1.00 eq) of *p*-cresol and 8.21 g (53.9 mmol, 1.05 eq) of 1-adamantanol were combined. While stirring, 3 mL of sulfuric acid (18 M) was added dropwise over a 15-min period. The reaction was allowed to stir for an additional 20 min before being with sodium hydroxide. Once the solution reached a pH of about 9, the mixture was washed three times with 50 mL portions of dichloromethane. The organic phase was dried with sodium sulfate. Evaporating off the solvent produced a white solid. Yield: 9.84 g (78.7%); ^{1}H NMR ($CDCl_3$, 300

MHz, δ, ppm): 7.01 (s, 1H), 6.86 (d, 1H, *J*= 1.5 Hz), 6.56 (d, 1H, *J*= 8.4 Hz), 4.57 (s, 1H), 2.27 (s, 5H), 2.12 (m, 12H), 2.08 (br s, 5H), 1.77 (br s, 11H).

2-adamantyl-4-methyl-6-(chloromethyl)phenol (3)

This procedures was conducted by a modification of a procedure from the literature.[7] Hydrogen chloride gas was created via addition of sulfuric acid to solid sodium chloride. The gas was generated in a 3-neck round bottom flask that was connected to an empty 3-neck round bottom flask via tubing. This empty flask was then connected to a glass pipet, via tubing, that was used to deliver the gas directly into the reaction solution present in the 3-neck round bottom reaction flask. In 17.5 mL of toluene, 6.24 g of 2-adamantyl-p-cresol **(2)** (25.8 mmol, 1.00 eq) was added to the reaction flask and the mixture was stirred. Hydrogen chloride gas was bubbled into the reaction mixture for 20 min. Then, 1.10 g of paraformaldehyde (36.6 mmol, 1.42 eq) was added in portions over a 15-min period. The hydrogen chloride gas was bubbled into the reaction flask for 50 min, in which the solid paraformaldehyde was no longer visible. The gas flow was halted and the reaction mixture stirred for an additional 40 min. The crude mixture was filtered and the collected crystals were washed with two portions of 10 mL cold water and one portion of 15 mL cold sodium bicarbonate to give product as a white powder. Yield: 0.78 g (10.4%); ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 7.05 (d, 1H, *J*= 2.1 Hz), 6.91 (d, 1H, *J*= 3.8), 5.36 (s, 1H), 4.66 (s, 2H), 2.28 (s, 4H), 2.19–2.12 (br m), 1.79 (br s, 10H).

Bis(mesitylimidazolium-ethyl)amine (4)

The procedure was conducted according to the literature.[4] To a schlenk flask, 2.21 g of bis(2-chloroethyl)amine hydrochloride (12.4 mmol, 1.00 eq) and 4.54 g of 1-(2,4,6-trimethylphenyl)-*1H*-imidazole **(1)** (24.4 mmol, 1.97 eq) were added with 15 mL of acetonitrile.

The reaction mixture was brought to reflux under nitrogen and continued to reflux for 3 d. The crude product mixture was condensed to give a highly viscous dark brown solid. This solid was then transferred into centrifuge tubes, about 3 mL of acetonitrile was added and the mixture was shaken vigorously. The tubes were then cooled to –35°C. Once the product precipitated out of the mixture, the tubes were centrifuged at 6000 rpm for 5 min, the then brown acetonitrile supernatant solution was decanted, and the process was repeated until the acetonitrile remained clear after mixing with the centrifuge pellet. This then gave a white solid as the pure product. Yield: 1.26 g (23.0%); ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 10.0 (s, 2H), 8.64 (s, 2H), 7.12 (s, 2H), 6.96 (s, 4H), 5.24 (br s, 4H), 4.02 (br s, 4H), 2.32 (s, 6H), 2.12 (s, 13H).

(H_3BIMPN^{Mes,Ad,Me})(BPh_4) (5)

Experimental procedure was conducted according to the literature.[4] In a schlenk flask containing 12 mL of dichloromethane, 0.81 g of bis(mesitylimidazolium-ethyl)amine **(4)** (1.82 mmol, 1.00 eq) was added, stirred, and the suspension turned clear. This mixture was then brought to reflux. A mixture of 0.47 g of 2-adamantyl-4-methyl-6-(chloroethyl)phenol **(3)** (1.62 mmol, 1.13 eq) in 4 mL of dichloromethane was added dropwise over 15 min. The reaction mixture refluxed overnight before being cooled to room temperature, filtered, and evaporated. The recovered crude product was dissolved in about 8 mL of methanol and heated to reflux. 0.942 g of tetraphenylborate in 4 mL of methanol was added to the refluxing reaction mixture causing the product to precipitate out. The precipitate was washed with about 200 mL of cold methanol and dried. The dry product was sonicated in 10 mL of ether, decanted, and dried again. This viscous white solid was combined with 8 mL of benzene in a flask and stirred for about 3 h before having the benzene decanted. The viscous white solid became more clear and less viscous. This final solid was dried to give a white solid. Yield: 0.50 g (26%); ^{1}H NMR ($CDCl_3$,

300 MHz, δ, ppm): 8.37 (br s), 7.33 (vbr s, 19H), 7.01 (m, 6H), 6.88 (t, 20H, *J*= 6.6 Hz), 6.79 (t, 11H, *J*= 6.9 Hz), 6.61 (br s, 1H), 5.76 (vbr s), 5.59 (br s, 1H), 3.40 (m), 3.16 (br m, 4H), 2.39 (br s, 11H), 2.35 (m), 2.24 (s, 3H), 2.09 (m, 10H), 1.77 (br m).

[(BIMPN^{Mes,Ad,Me})Co^{II}]Cl (7)

All procedures were conducted in a glove box and according to the literature.[4] In a small vial, 0.10g of (H_3BIMPN^{Mes,Ad,Me})(BPh_4) **(5)** (0.075 mmol, 1.1 eq) and about 2 mL of THF were combined. In a separate small vial, 0.024 g (0.25 mmol, 3.7 eq) of potassium t*ert*-butoxide and about 1 mL of THF were combined. The two vials were put in the glove box cold-well. The cold-well was prepared using isopropanol and dry ice. The vials remained in the cold-well for 1.5 h. The contents of the vials were then combined into one vial and left in the cold well for 2 h. After this time, the vial was left at room temperature to stir overnight. The resulting mixture was filtered through a Celite glass-pipet filter and into a vial containing 0.0088g of cobalt(II) chloride (0.068 mmol, 1.0 eq). This mixture was left to stir overnight. The contents of the vial were then evaporated. About 3 mL of benzene was added to the solid and the mixture was left to stir overnight. Filtration of the resulting mixture through a celite glass-pipet and recovery of the residue with acetonitrile yielded a green solution. The solvent was evaporated and the cobalt(II) chloride was recovered. ^{1}H NMR ($CDCl_3$, 300 MHz, δ, ppm): 54.93 (br s), 53.85 (br s), 21.84 (br s), 6.70 (s), 6.42 (s), 5.50 (s), 1.98 (s), 0.74 (s), -1.20 (s), -2.06 (br s), -3.98 (s).

CHAPTER III

RESULTS AND DISCUSSION

2-adamantyl-4-methyl-6-(chloromethyl)phenol **3** was successfully prepared by a sequence of two S_N1 alkylations of *p*-cresol, followed by introduction of a chloromethyl substituent under the action of HCl gas. Bis(mesitylimidazolium-ethyl)amine **4** was successfully made by generating the mesitylimidazolium, followed by a S_N2 reaction with bis(2-chloroethyl)amine. The preparation of $(H_3BIMPN^{Mes,Ad,Me})(BPh_4)$ **5** was successfully completed via the reaction of 2-adamantyl-4-methyl-6-(chloromethyl)phenol and Bis(mesitylimidazolium-ethyl)amine in the presence of tetraphenylborate. The $[(BIMPN^{Mes,Ad,Me})Co^{II}]Cl$ **7** ligand was synthesized in an inert atmosphere by deprotonation of $(H_3BIMPN^{Mes,Ad,Me})(BPh_4)$, followed by the addition of cobalt(II) chloride.

Throughout synthesis, several challenges arose and were subsequently overcome. One of the first challenges was purification of the bis(mesitylimidazolium-ethyl)amine **(4)**. The experiment was conducted as described in the literature.[4] However, the purification described by the literature was not successfully reproduced. In order to purify the compound, the centrifugation technique had to be incorporated. The desired compound was soluble in the product mixture, but insoluble in acetonitrile. Thus, the mixture was concentrated and acetonitrile was added then immediately removed (containing the desired product). The next major complication arose with the synthesis of 2-adamantyl-4-methyl-6-(chloromethyl)phenol **(3)**. Since hydrogen chloride gas was unavailable at the time of the experiment, the gas had to be created using solid sodium chloride and concentrated sulfuric acid. The 3-neck round bottom flask containing the sodium chloride had two opening closed using rubber septa and the third

was connected to tubing with a glass adaptor. This tubing led to an empty and much smaller 3-neck round bottom flask. This flask was put into place to insure the reaction mixture did not flow from the reaction flask to the sodium chloride flask. The trap flask had the top opening closed with a rubber septum. The other opening contained a glass adaptor that was used to run tubing from this empty trap flask to the reaction flask. This gas line was connected to a glass pipet that was inserted into the reaction flask, through a rubber septum, and into the reaction solution. The reaction 3-neck round bottom flask had the top opening sealed with a rubber septum and the last opening contained a glass adaptor to run tubing into an Erlenmeyer flask containing solid sodium hydroxide. This glassware setup is illustrated by figure 4. The concentrated sulfuric acid

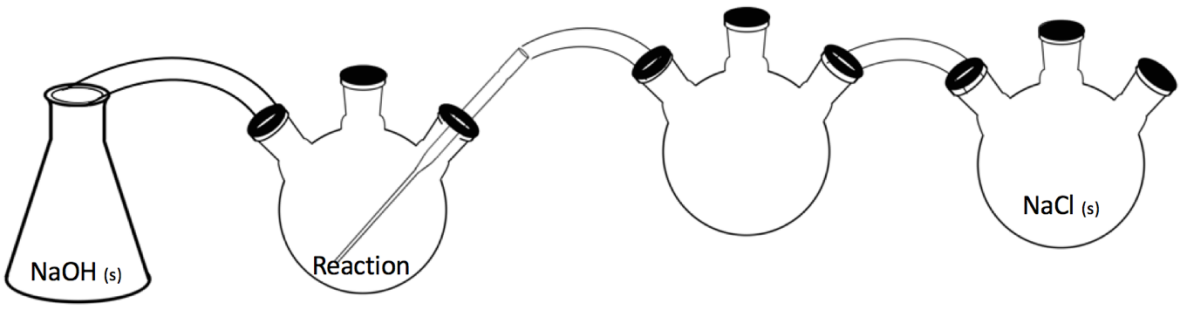


Figure 4. The glassware arrangement used to bubble hydrogen chloride gas into the reaction solution. Sizes are not to scale.

was added using a glass syringe through the rubber septum of the sodium chloride 3-neck round bottom flask. The production of hydrogen chloride gas was successful, but was not continuous at all times. There were several leaks that occurred during the reaction time that decreased gas flow into the solution. This is believed to have played a role in the low yield from this reaction.

Characterization of the multiple compounds and complexes via ^{1}H NMR were compared to the corresponding literature of each product. The only exception is 2-adamantyl-4-methyl-6-

(chloromethyl)phenol **(3)**. This compound was previously synthesized and characterized by ^{1}H NMR and X-ray crystallography. The single crystal X-ray diffraction identified the product to be 2-adamantyl-4-methyl-6-(chloromethyl)phenol and thus the ^{1}H NMR was used as a reference (see supporting information for ^{1}H NMR spectrum). There were several instance in which the integration of the experimentally determined peaks of multiple products were not as those from the literature. All of these integration calculation resulted in larger numbers than those of the corresponding literature. This was caused due to impurity peaks mixing with product peaks. These errors are listed by the compound's name followed the chemical shifts of the peaks and the correct integration: 2-adamantyl-p-cresol **(2)**, 2.27 (3H), 2.12 (6H), 2.08 (3H), and 1.77 (6H);[6] 2-adamantyl-4-methyl-6-(chloromethyl)phenol **(3)**, 2.28 and 1.79; bis(mesitylimidazolium-ethyl)amine **(4)**, 5.24 (2H), 4.02 (2H), and 2.12 (12H);[4] ($H_3BIMPN^{Mes,Ad,Me}$)(BPh_4) **(5)**, 7.33 (16H), 7.01 (4+1H), 6.88 (16H), 6.79 (8H), 5.59 (2H), 2.39 (6H), 2.35 (4H), 2.09 (6H), 1.77 (12H).[4] Even though there are different integration values for some of the peaks, the values are close to the literature values and are deemed within experimental error tolerations.

After the successful synthesis of the cobalt(II) chloride, synthesis began for the cobalt(II) azide. After ^{1}H NMR and IR had been conducted on the synthesized complex, it was believed to have contained the cobalt(II) azide. When single-crystal X-ray diffraction was conducted on the complex believed to be the cobalt(II) azide (see supporting information), it showed the cobalt complex losing its chloride and binding to the nitrogen atom nearby. Tetraphenyl borate was also interacting with the complex to balance charge. However, there was no bound azide. This result deemed the cobalt(II) azide synthesis to be unsuccessful.

A sample of [($BIMPN^{Mes,Ad,Me}$)$Co^{II}(N_3)$] that had been previously prepared (by Breanna Lily) was recrystallized. These blue crystals were then analyzed via X-ray crystallography.

However, the crystals did not diffract any of the X-rays, making it impossible to be characterized nor could experimentation be done on the sample.

CHAPTER IV

CONCLUSION

With the success in synthesizing the [(BIMPN^{Mes,Ad,Me})Co^{II}]Cl, but not being able to synthesize the cobalt azide, there must have been a flawed procedure in azide synthesis. There had been multiple attempts to generate very pure cobalt chloride complexes. Once a very pure chloride had been synthesized, the azide reaction was attempted on a small scale. However, the small scale resulted in too little product and azide was unable to be characterized.

The uncertainty in the final results for the cobalt azide did not eliminate any hopes of future synthesis. However, the attempts that had been made thus far were unsuccessful. Since the hypothesis being tested was whether solid-state photolysis of the cobalt azide would generate a cobalt nitrido, the hypothesis has not yet been evaluated. Future corrections that could be implemented to synthesize the cobalt azide include synthesizing pure cobalt chloride and scaling up the azide reaction. With the synthesis of the cobalt azide, the hypothesis would then be able to be tested.

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